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THE SHRINKAGE OF EPOXY BONDING AGENTS
IN THE CURING PROCESS

V. V. Bolitin, et al

Royal Aircraft Establishment
Farnborough, England

1972

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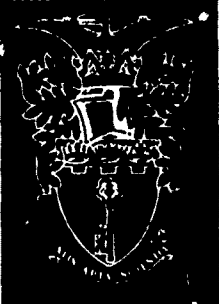
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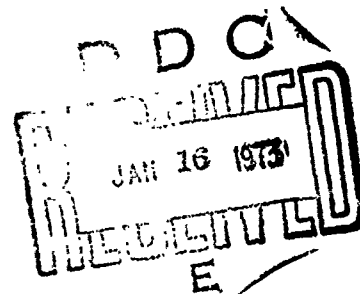
by

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THE SHRINKAGE OF EPOXY BONDING AGENTS IN THE CURING PROCESS
(OB USADKE EPOKSIDNYKH SVYAZUYUSHCHIKH V PROTSESSE OTVERZHDENIYA)

by

V. V. Bolotin

K. S. Bolotina

Mekh. Polimerov, 192, 1, 178-181 (1972)

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AUTHORS' SUMMARY

This paper reports the results of measurements of the density of two types of epoxy bonding agents in the process of hardening (curing) from the initial liquid state to the final state at room temperature. The part played by heat shrinkage in overall shrinkage deformation is evaluated. It is shown that the shrinkage factor in relation to the state with the least density exceeds the values cited in the literature. The paper contains 6 Figures and 7 References.

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It is known¹ that the residual stresses arising in articles made of glass-fibre reinforced plastics are determined to a considerable extent by heat shrinkage of the bonding agent as it cools from the curing temperature to the service temperature. The part played by chemical shrinkage in the formation of residual stresses is less clear. Some findings obtained by the use of strain gauges bonded into coil-wound articles have been published in Ref.2. Calculation of residual stresses requires a knowledge of the entire process of the density changes occurring in the bonding agent in time, since the stresses which arise in the early stages of curing undergo relaxation. The published data, however, relate only to the final values for shrinkage and are frequently contradictory. Alongside values of 1.5 - 2.5% (see Ref.3 for example) there are indications⁴ that the shrinkage of epoxy bonding agents may be as much as 10% or even more. In so far as these data are usually cited with no indication of the curing regime or of the state for which the change of volume has been calculated it is not possible to use them in calculations. The purpose of the present work is to study the process of density changes in epoxy bonding agents throughout the entire hardening process. The conventional methods of measuring shrinkage are either unsuitable for this purpose or else give rise to considerable error. In this study we used a technique of hydrostatic weighing in a liquid which at the same time played the part of a heat-regulating medium^{5,6}.

A weighed amount of bonding agent (about 100 g) was heated to 60°C, carefully stirred, poured into a rubber container with walls about 50 μ m thick and kept in this until all bubbles had disappeared. The container was then pinched off and hermetically sealed below the level of the liquid and the remainder of the liquid was poured off. The absence of bubbles was checked by visual observation. The sample thus obtained was cooled in air to 20°C and then weighed in air and water to determine the initial density of the bonding agent. Heat treatment and further weighing were carried out in pure glycerine (State Standard 6259-52). As in certain stages of heat treatment the density of the bonding agent is less than that of glycerine small steel weights were attached to the samples. The vessel containing glycerine was put in a laboratory drying cabinet and heated while being carefully stirred. The samples were weighed at 15 - 30 minute intervals to an accuracy of 50 mg. The temperature was measured to an accuracy of 1°C. Heat treatment was stopped overnight, the samples being cooled in air to room temperature and then weighed in air and in water. This weighing was also carried out at the

end of the experiment. The tightness of the container seal was checked both by visual observation and by weighing the samples. Samples which had not withstood the heat treatment were eliminated from the experiment. The density of the bonding agent was calculated from the measured weight in air, water and glycerine. The temperature dependence of the density of glycerine, rubber and steel were taken into account in the calculations. In all about 10^5 measurements were made. The results were processed on a 'Minsk-22' electronic computer.

Some of the results relating to epoxy resin type A are shown in Figs.1-4. TEAT was used as the hardening agent in the proportion of 15 parts by weight of TEAT to 100 parts by weight of resin. The actual regime of heat treatment for four samples is shown in Fig.1. The heat treatment included about 3 hours at 100°C and about 12 hours at 150°C . There was a break in heat treatment after 12 hours. The overall duration of the experiment was about 24 hours.

Fig.2 shows the changes in the density ρ of the bonding agent versus time. The complex nature of the dependence is due to the superposition of the curing process on the purely thermal volume changes. In the first stage ($0 < t < 2.5$ h) the density decreases since the predominant factor is thermal expansion linked with temperature build-up to $T = 100^{\circ}\text{C}$. This is followed by intensive chemical shrinkage. The second and third density minima (which occur about 7 and 10 hours after heat treatment is begun) are associated with transition to the regime $T = 150^{\circ}\text{C}$. Overnight cooling makes it possible to distinguish the purely thermal component of shrinkage. After heating for the second time practically the same density values are obtained; the process of chemical shrinkage has already slowed down to a considerable extent. The density of the cooled bonding agent after 12 and 24 hours of heat treatment is practically the same.

The curves of density change versus time fully describe the process of shrinkage for the given regime of heat treatment. Usually^{3,4,7} the density changes are characterised by means of a shrinkage factor (expressed as a percentage). Shrinkage is calculated with respect to a certain initial state which is not precisely defined. For example, when shrinkage is measured with a wire-type resistance strain gauge the latter begins to react to the deformation of the resin when a certain depth of curing is attained. At the same time in the mass of the resin a stress/strain state arises which changes in time not only as a result of shrinkage but also in consequence of rheological processes. In our method the initial state is also fairly arbitrary but is

capable of precise definition. If shrinkage is measured with reference to the liquid state before heat treatment is started, then in the early stages of heat treatment we shall have a negative shrinkage factor. A more natural procedure is to measure shrinkage with respect to the state having the least density. This state is the yield state. It begins soon after the onset of heat treatment. The volume shrinkage factor.

$$\theta = 1 - \frac{\rho_{\min}}{\rho}, \quad (1)$$

will in this case be a positive value. Here ρ_{\min} is the minimum density found in the curing process. Hereafter we shall take the expression 'shrinkage factor θ ' to mean the parameter defined in accordance with (1). The graph for the factor θ is shown in Fig.3. The qualitative inferences concerning the change of the shrinkage factor with time are analogous to those which were drawn with regard to the density ρ . The final value of the shrinkage factor θ is over 9%. This corresponds to the linear shrinkage factor which exceeds 3%. Lower values are usually quoted in the literature³. The differences would appear to be due to the fact that these values are calculated with reference to a fairly hardened state whereas we calculate the shrinkage factor with respect to the state having the least density.

It is usual to distinguish the chemical and thermal components of shrinkage. Insofar as the coefficient of thermal expansion of the bonding agent changes in the curing process, and the measurement of this coefficient is inevitably associated with curing, this distinction is somewhat formal. If by the chemical shrinkage factor we understand the relative volume decrease at the end of the curing process (i.e. before cooling begins), then this factor amounts to about 3%. Since the minimum density is attained at $T \approx 100^{\circ}\text{C}$ this factor also includes the purely thermal expansion associated with transition from one regime to another. In order to exclude the influence of thermal expansion it is necessary to compare the density before and after curing at the same temperature. In this case the volume coefficient of chemical shrinkage turns out to be equal to approximately 6% or more. This is clear from Fig.4, for example, where for one of the samples the parametric dependence of the density on temperature during the first 12 hours of curing is shown. As far as the thermal component of shrinkage after curing is concerned, in the temperature interval of $20 - 150^{\circ}\text{C}$ this amounts to about 5.5%, or in terms of the mean coefficient of linear thermal expansion in the same temperature interval

$\alpha \approx 15 \times 10^{-5}/^{\circ}\text{C}$. This is in agreement with data obtained using a quartz dilatometer.

Analogous results for an epoxy bonding agent based on compound type B are shown in Figs.5 and 6. The hardening agent was TEAT used in the proportion of 10 parts by weight per 100 parts by weight of resin. The qualitative inferences are analogous to those cited above for bonding agent A. The values of the shrinkage factor for B are somewhat lower than those for bonding agent A.

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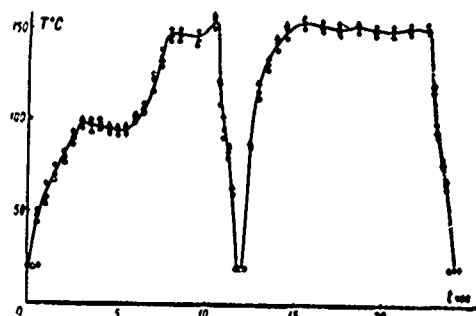


Fig.1

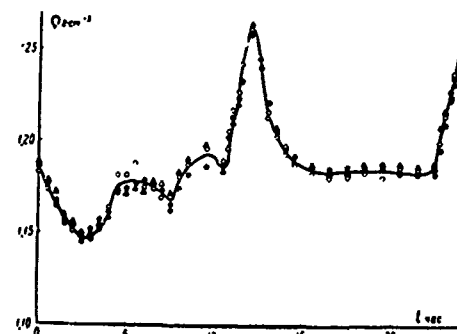


Fig.2

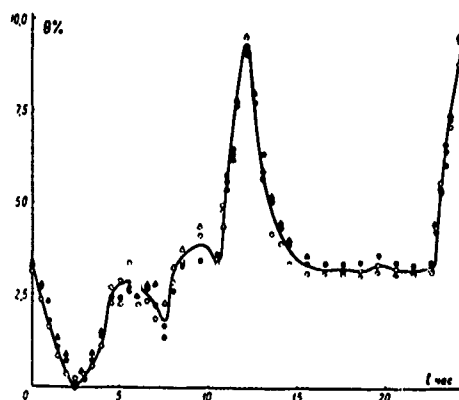


Fig.3

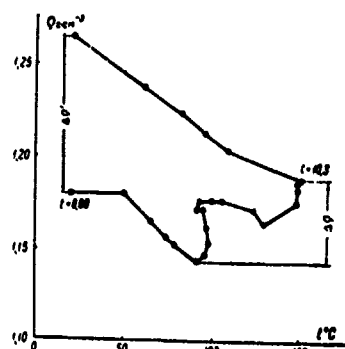


Fig.4

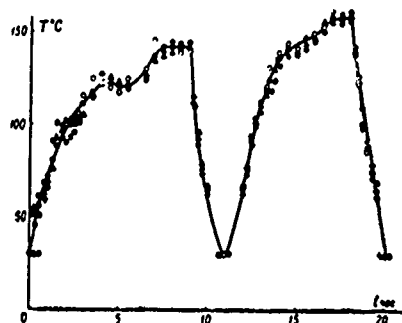


Fig.5

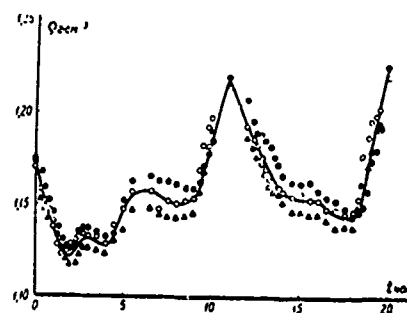


Fig.6

Fig.1-6